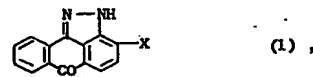


(12) UK Patent Application (19) GB (11) 2 003 477 A

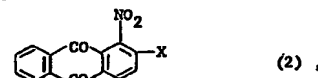
- (21) Application No 7835369
(22) Date of filing 1 Sep 1978
(23) Claims filed 1 Sept 1978
(30) Priority data
(31) 10735/77
737/78
(32) 2 Sep 1977
24 Jan 1978
(33) Switzerland (CH)
(43) Application published
14 Mar 1979
(51) INT CL²
CO7D 231/64
(52) Domestic classification
C2C 1405 213 247 250 252
25Y 305 30Y 351 352 366
367 368 387 625 628 678
760 TY
(56) Documents cited
None
(58) Field of search
C2C
(71) Applicant
Ciba-Geigy AG,
4002 Basle,
Switzerland,
(72) Inventor
Anthanasios Tzikas
(74) Agent
Messrs. J.A. Kemp and
Co.

(54) Process for the production of 3-substituted pyrazolanthrones

(57) A process for the production of 3-substituted pyrazolanthrones of the formula



wherein X is C_1 - C_6 alkyl, C_1 - C_6 alkoxy or a group -COR, in which R is hydrogen, C_1 - C_6 alkyl, hydroxyl, C_1 - C_6 alkoxy, -NH₂, -NH- C_1 - C_6 alkyl or -NR₁R₂, in which R₁ and R₂, each independently of the other, are C_1 - C_6 alkyl, which comprises reacting 1-nitroanthraquinones of the formula



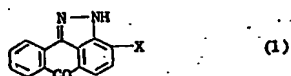
wherein X is as defined in formula (1), in aprotic dipolar solvents, with hydrazine or hydrazine hydride, at normal or slightly elevated temperature, to give 3-substituted pyrazolanthrones of the formula (1), which we dyestuff intermediates

GB2 003 477 A

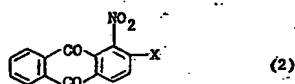
SPECIFICATION

Process for the production of 3-substituted pyrazolanthrone

The present invention relates to a process for the production of 3-substituted pyrazolanthrone of the formula



wherein X is C₁-C₆alkyl, C₁-C₆alkoxy or a group -COR, in which R is hydrogen, C₁-C₆alkyl, hydroxyl, C₁-C₆alkoxy, -NH₂, -NH-C₁-C₆alkyl or -NR₁R₂, in which R₁ and R₂, each independently of the other, are C₁-C₆alkyl, which comprises reacting 1-nitroanthraquinones of the formula



wherein X is as defined in formula (1), in aprotic dipolar solvents, with hydrazine or hydrazine hydride, at normal or slightly elevated temperature, to give 3-substituted pyrazolanthrone of the formula (1).

The substituent X in formulae (1) and (2) can be for example: methyl, ethyl, propyl, isopropyl, butyl, hexyl, methoxy, ethoxy, propoxy, isopropoxy, butoxy, formyl, acetyl, propionyl, carboxyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, carbamoyl, N-methylcarbamoyl, N-ethylcarbamoyl, N,N-dimethylcarbamoyl and N,N-diethylcarbamoyl.

As starting compounds of the formula (2), there may be mentioned in particular: 1-nitro-2-methylanthraquinone, 1-nitro-2-ethylanthraquinone and 1-nitro-2-carboxyanthraquinone.

Examples of suitable aprotic dipolar solvents which may be used in the process of the invention are: N-methyl-2-pyrrolidone, tetramethylurea, sulfolane, hexamethylphosphoric triamide, dimethyl sulfoxide, dimethyl acetamide, diethyl acetamide, acetonitrile, dimethyl formamide, 3,3'-thiodipropionitrile and also pyridine.

The most advantageous reaction temperature depends on the starting compound and the solvent employed. Thus the reaction can often be carried out at room temperature. During the reaction, the temperature of the reaction mixture generally rises to 30° to 40°C. The reaction can also be initiated above room temperature (e.g. at 30°C) or below it (e.g. at 5° to 10°C). The advantageous temperature range for the process of the invention is that between about 0° and 100°C.

A preferred embodiment of the process of the invention consists in reacting 1-nitro-2-methylanthraquinone, 1-nitro-2-ethylanthraquinone or 1-nitro-2-carboxyanthraquinone in N-methyl-2-pyrrolidone, sulfolane or dimethyl sulfoxide, with hydrazine hydrate, to give 3-methylpyrazolanthrone, 3-ethylpyrazolanthrone or 3-carboxy-

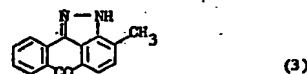
In the course of the process of the present invention, there is probably formed as intermediate the corresponding 2-substituted 1-hydrazinoanthraquinone, which is immediately cyclised to the pyrazolanthrone.

The 3-substituted pyrazolanthrone of the formula (1) are important intermediates for the production of valuable vat dyes, pigments and disperse dyes.

The invention is illustrated by the following Examples in which the parts are by weight.

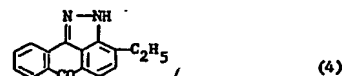
Example 1

16 parts of 1-nitro-2-methylanthraquinone are suspended in 140 parts of N-methyl-2-pyrrolidone. The suspension is heated to 85°C and, at this temperature, a solution of 3.2 parts of hydrazine hydrate in 40 parts of N-methyl-2-pyrrolidone are added dropwise in the course of 20 minutes. The reaction mixture is then stirred for 5 minutes, cooled to room temperature and filtered. The filter residue is non-reacted starting material (3 parts). Water is added to the filtrate, which is then filtered. The residue is washed neutral with water. Yield: 12 parts of 3-methylpyrazolanthrone of the formula



Example 2

10 parts of 1-nitro-2-ethylanthraquinone are suspended at room temperature in 50 parts of sulfolane. The suspension is heated to 55°C and, at this temperature, 4 parts of hydrazine, dissolved in 20 parts of sulfolane, are added dropwise in the course of 2 hours. The reaction mixture is stirred for 10 minutes and filtered after the addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water. Yield: 9 parts of 3-ethylpyrazolanthrone of the formula



Example 3

10 parts of 1-nitro-2-ethylanthraquinone are suspended at room temperature in 50 parts of N-methyl-2-pyrrolidone. The suspension is heated to 60°C and, at this temperature, 4 parts of hydrazine hydrate, dissolved in 20 parts of N-methyl-2-pyrrolidone, are added dropwise in the course of 2 hours. The reaction mixture is stirred for 10 minutes and filtered after the addition of 200 parts of mixture of ice and water. The filter cake is washed neutral with water. Yield: 8.5 parts of 3-ethylpyrazolanthrone of the formula (4).

10 parts of 1-nitro-2-ethylanthraquinone are suspended at room temperature in 60 parts of sulfolane. Then 4 parts of hydrazine hydrate, dissolved in 20 parts of sulfolane, are added dropwise to this suspension in the course of 2 hours. The

reaction mixture is then stirred for 10 minutes and filtered after the addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water. Yield: 8.5 parts of 3-ethylpyrazolanthrone of the formula (4).

Example 5

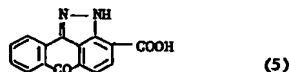
10 parts of 1-nitro-2-ethylantraquinone are suspended at room temperature in 60 parts of N-methyl-2-pyrrolidone. Then 4 parts of hydrazine hydrate, dissolved in 20 parts of N-methyl-2-pyrrolidone, are added dropwise to this suspension in the course of 2 hours. The reaction mixture is then stirred for 10 minutes and filtered after the addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water. Yield: 8.2 parts of 3-ethylpyrazolanthrone of the formula (4).

Example 6

10 parts of 1-nitro-2-ethylantraquinone are suspended at room temperature in 50 parts of dimethyl sulfoxide. The suspension is heated to 55°-60°C and, at this temperature, 4 parts of hydrazine hydrate, dissolved in 200 parts of dimethyl sulfoxide, are added dropwise in the course of 2 hours. The reaction mixture is then stirred for 10 minutes and filtered after the addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water. Yield: 9 parts of 3-ethylpyrazolanthrone of the formula (4).

Example 7

10 parts of 1-nitro-2-carboxyanthraquinone are suspended at room temperature in 50 parts of sulfolane. The suspension is heated to 55°C and, at this temperature, 4 parts of hydrazine hydrate, dissolved in 20 parts of sulfolane, are added dropwise in the course of 2 hours. The reaction mixture is stirred for 10 minutes and filtered after the addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water. Yield: 9 parts of 3-carboxypyrazolanthrone of the formula



Example 8

10 parts of 1-nitro-2-carboxyanthraquinone are suspended at room temperature in 50 parts of N-methyl-2-pyrrolidone. The suspension is heated to 50°C and, at this temperature, 4 parts of hydrazine hydrate, dissolved in 20 parts of N-methyl-2-pyrrolidone, are added dropwise in the course of 2 hours. The reaction mixture is then stirred for 10 minutes and filtered after the addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water. Yield: 8.5 parts of 3-carboxypyrazolanthrone of the formula (5).

Example 9

10 parts of 1-nitro-2-carboxyanthraquinone are suspended at room temperature in 60 parts of N-methyl-2-pyrrolidone. Then 4 parts of hydrazine hydrate, dissolved in 20 parts of N-methyl-2-pyrrolidone, are added dropwise to this suspension in the course of 2 hours. The reaction

addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water and dried. Yield 8.4 parts of 3-carboxypyrazolanthrone of the formula (5).

Example 10

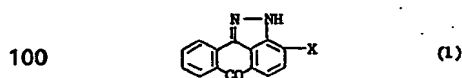
10 parts of 1-nitro-2-carboxyanthraquinone are suspended at room temperature in 60 parts of sulfolane. Then 4 parts of hydrazine hydrate, dissolved in 20 parts of sulfolane, are added dropwise to this suspension in the course of 2 hours. The reaction mixture is then stirred for 10 minutes and filtered after the addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water. Yield: 8.6 parts of 3-carboxypyrazolanthrone of the formula (5).

Example 11

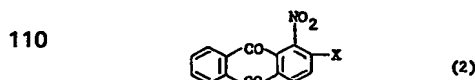
10 parts of 1-nitro-2-carboxyanthraquinone are suspended at room temperature in 50 parts of dimethyl sulfoxide. The suspension is heated to 55°-60°C and at this temperature 4 parts of hydrazine hydrate, dissolved in 20 parts of dimethyl sulfoxide, are added dropwise to this suspension in the course of 2 hours. The reaction mixture is then stirred for 10 minutes and filtered after the addition of 200 parts of a mixture of ice and water. The filter cake is washed neutral with water. Yield: 9 parts of 3-carboxypyrazolanthrone of the formula (5).

CLAIMS

1. A process for the production of 3-substituted pyrazolanthrone of the formula



wherein X is C₁-C₆alkyl, C₁-C₆alkoxy or a group -COR, in which R is hydrogen, C₁-C₄alkyl, hydroxyl, C₁-C₆alkoxy, -NH₂, -NH-C₁-C₆alkyl or -NR₁R₂, in which R₁ and R₂, each independently of the other are C₁-C₆alkyl, which comprises reacting 1-nitroanthraquinones of the formula



wherein X is as defined in formula (1), in aprotic dipolar solvents, with hydrazine or hydrazine hydrate, at normal or slightly elevated temperature, to give 3-substituted pyrazolanthrone of the formula (1).

2. A process according to claim 1, wherein 1-nitro-2-methylantraquinone, 1-nitro-2-ethylantraquinone or 1-nitro-2-carboxyanthraquinone is reacted in N-methyl-2-pyrrolidone, sulfolane or dimethyl sulfoxide, with hydrazine hydrate, to give 3-methylpyrazolanthrone, 3-ethylpyrazolanthrone or 3-carboxypyrazolanthrone.

3. The 3-substituted pyrazolanthrone obtained by the process according to claims 1 and 2.

4. A method of producing vat dyes, pigments

3-substituted pyrazolanthrones obtained by the process according to claims 1 and 2.

5. A process according to claim 1 or 2 which is carried out at a temperature of 0 to 100°C.

5 6. A process according to claim 1 substantially as hereinbefore described.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon Surrey, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.